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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF
MAGNESIUM.

BY THEODORE WILLIAM RICHARDS AND HARRY GEORGE PARKER.

Presented May 18, 1896.

ALTHOUGH numerous determinations of the atomic weight of magnesium have been made, the results obtained show such very wide variations among themselves that the value in use at present cannot be accepted with any certainty. It will not be necessary to review in detail all the work published, as most of it was done more than forty years ago, before quantitative methods had attained their present exactness; but the following table of methods used and results obtained will assist in a clear comprehension of the situation.

PREVIOUS WORK ON THE ATOMIC WEIGHT OF MAGNESIUM.*

Synthesis of sulphate by the action of sulphuric acid on the oxide.

Berzelius, 1826. Lehrbuch, 5th edition, III. 1227 25.3

Svanberg and Nordenfeldt, 1848. Erdmann's Journ.

Prak. Chem., 1848, XLV. 473 24.7

Bahr, 1852. Erdmann's Journ. Prak. Chem., 1852,

LVI. 310 24.8

Marignac, 1884. Annal. Chim. Phys., 1884, (5.), I.

289, 321 24.37

Conversion of sulphate into oxide.

Jacquelain, 1851. Annal. Chim. Phys., (3.), XXXII.

195 24.5

Determination of sulphuric acid in sulphate.

Gay-Lussac, 1820. Annal. Chim. Phys., XIII. 308 24.6

* We are indebted to F. W. Clarke for most of the above references.

| | |
|------------------------------------------------------------------------------|-------|
| Scheerer, 1846. Poggend. Ann., 1846, LXIX. 535 | 24.5 |
| Scheerer, 1847, Later Correction. Poggend. Ann., 1847, LXX. 407 | 24.5? |
| Jacquelain, 1851. Annal. Chim. Phys., 1851, (3.), XXXII. 195 | 24.2 |
| Conversion of oxalate into oxide. | |
| Svanberg and Nordenfeldt, 1848. Erdmann's Journ. Prak. Chem., 1848, XLV. 473 | 24.7 |
| Determination of chlorine in magnesic chloride. | |
| Dumas, 1859. Ann. Chim. Phys., 1859, (3), LV. 129, 187 | 24.6 |
| Conversion of carbonate into the oxide. | |
| Marchand and Scheerer, 1850. Erdmann's Journ. Prak. Chem., 1850, L. 385 | 24.0 |
| Scheerer, 1859, Later Correction. Liebig's Ann., 1859, CX. 236 | 24.0 |
| Conversion of metal into oxide. | |
| Burton and Vorce, 1890. Am. Chem. Journ., 1890, XII. 219 | 24.29 |

It will be seen that, with the exception of the results obtained by the precipitation of the sulphuric acid with barium chloride and the precipitation of the chlorine with argentic nitrate, all the methods employed involve the use of magnesic oxide. The fact that all such results are untrustworthy was shown by T. W. Richards and E. F. Rogers* in their work upon the occlusion of gases by the oxides of certain metals when obtained by the ignition of various salts. The error from this source is so large that it seems hopeless to apply a correction to previous work upon the atomic weight of magnesium, as the amount of gas occluded depends in a large degree upon the method and thoroughness of ignition.

Concerning the results obtained by the precipitation of the sulphuric acid in magnesic sulphate, it is only necessary to point out the error due to the occlusion of various soluble substances present in the solution from which the precipitation was made. This error was recognized by Scheerer, after publishing his results, and an approximate correction was made; but such a correction does not merit much confidence, as will be seen.

In the work of Dumas it is evident that some magnesic oxychloride

* These Proceedings, Vol. XXVIII. p. 200.

was formed, and he does not appear at all confident of the accuracy of his results. From the experience of the writers it does not seem likely that the method which he used would give magnesic chloride free from the oxide.

PRELIMINARY EXPERIMENTS.

Because considerable experience had been gained in a previous research,* upon the occlusion by baric sulphate of salts present in a solution from which this insoluble salt was precipitated, it was thought that Gay-Lussac's and Scheerer's method of precipitating magnesic sulphate with baric chloride might now be used with advantage, applying subsequently the necessary corrections for occluded substances. It had previously been found that the concentration of the solution and the method of pouring had a great deal to do with the amount of occlusion; and hence it seemed likely that, by working in a very dilute solution and pouring the magnesic sulphate into the baric chloride with extreme slowness, the occlusion of baric chloride might be large, but that the precipitate might be free from magnesium. Several experiments were made to ascertain the correctness of this supposition, but in each case it was found that, notwithstanding the precautions adopted, a very notable quantity of magnesium was occluded in the baric sulphate. It had been the custom in working upon this precipitation to fuse the weighed baric sulphate with sodic carbonate, to extract the sodic chloride thus formed, and to determine the chlorine with argentic nitrate and calculate as baric chloride, subtracting this amount from the total weight of baric sulphate found. This method gave very satisfactory results, but of course it could not be applied when the baric sulphate was mixed with magnesic chloride and sulphate as well as baric chloride, for then no one could discover the proportion in which each salt was present, with sufficient accuracy for work upon atomic weights.

The possibility of obtaining satisfactory results by the determination of the chlorine in magnesic chloride was now considered. The great disadvantage of this method, as is well known, is the extreme difficulty of obtaining pure anhydrous magnesic chloride. The usual method of igniting the double chloride of ammonium and magnesium was tried a number of times, but it was found that a quantity of the oxychloride was always formed. As indicators do not give a sharp reaction in the presence of magnesic salts, the hydrochloric acid driven off cannot be added

* These Proceedings, Vol. XXXI. p. 67.

afterwards by titrating back to the neutral point with a weak acid solution, and it is therefore necessary to obtain in the first place magnesic chloride containing its full complement of acid.

The method was then modified by conducting the ignition of the double salt in a tightly covered platinum crucible in a stream of hydrochloric acid, instead of air. That a considerable quantity of oxychloride was usually formed, even under these conditions, was easily ascertained by dissolving the resulting product in water, when the oxychloride remained as an insoluble residue. In two or three cases, however, the amount of oxychloride formed was comparatively small; hence it was hoped that, if the right conditions could be found, the chloride might be obtained in a pure state. Another series of experiments with a modified apparatus was therefore undertaken. The expulsion of the ammonic chloride was conducted in a combustion tube and the number of drying tubes was increased, so that the hydrochloric acid gas might be as free as possible from water. The heat was applied very gradually, in order that the double chloride might be almost anhydrous before the sublimation of the ammonic chloride began. This method gave better results. It was observed that in two or three experiments, where the conditions had been unusually favorable, the resulting chloride gave a clear solution; and it seemed therefore probable that, if an apparatus could be devised to deliver a rapid stream of hydrochloric acid gas entirely free from aqueous vapor, the method might be successful.

Assuming that these conditions might be fulfilled, another difficulty remained to be overcome; for even if the magnesic chloride could be obtained in the combustion tube free from water and oxychloride, the problem still remained to weigh the salt without foreign admixture. If the boat were allowed to remain in the tube until cool, and then removed to a weighing bottle, the salt must absorb a very notable quantity of moisture from the air in the operation, however quickly this operation might be performed. The boat cannot be transferred to another tube and reheated, as the moisture present reacts upon the chloride, forming some oxychloride and liberating hydrochloric acid. If it is taken from the combustion tube while hot and allowed to cool in a weighing bottle, the same effect is produced. Dumas had met with the same difficulties in his work with this method, and he endeavored to compromise matters by removing the boat from the combustion tube when it had only partly cooled. As his subsequent results proved, however, the moisture from the air reacted upon the chloride, forming some oxychloride, which interfered seriously with the accuracy of his work. To obviate this

difficulty the form of apparatus used by one of us* in drying strontic bromide was altered so that the boat could be transferred directly from the ignition tube to the weighing bottle without an instant's exposure to the outside air. In order to accomplish this result the hard glass tube was ground with a long tapering joint directly into the wider desiccating or cooling tube used to contain the weighing bottle. This desiccating tube had a sort of bulb or "pocket" blown upon one side of it, to receive the stopper of the weighing bottle, thus allowing the boat to be pushed past the stopper directly from the ignition tube into the bottle. Afterwards the stopper could be rolled into place with a rod provided for the purpose. The arrangement was used with great success in a recent determination of the atomic weight of zinc,† to which it was equally applicable. A reference to the annexed sketch will make the apparatus more comprehensible.

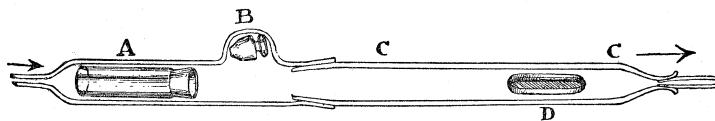


FIG. 1.— BOTTLING APPARATUS, HORIZONTAL SECTION.

A = weighing bottle. B = stopper of bottle. C C = hard glass tube.
D = Platinum boat containing fused magnesic chloride.

The desiccating apparatus for the hydrochloric acid gas consisted of two towers, composed of a number of glass bulbs filled with beads, upon which strong sulphuric acid was allowed to trickle from small reservoirs at the top into suitable receptacles at the bottom. This apparatus was constructed wholly of glass, with glass gridirons for flexibility, and ground or sealed glass connections. Joints were made tight with syrupy phosphoric acid (Morley). The hydrochloric acid, after being evolved by allowing strong sulphuric acid to run into a flask containing a strong solution of hydrochloric acid, was passed through a wash bottle containing sulphuric acid, thence through the towers just described, afterwards through a tube containing phosphoric pentoxide, and finally into the combustion tube. The apparatus was so arranged that the current of air from an aspirator could be passed through another set of towers, a duplicate of those used for drying the acid gas. By means of stopcocks either dry

* Richards, These Proceedings, XXX. 383.

† Richards and Rogers, These Proceedings, XXXI. 158, 174.

hydrochloric acid gas or dry air could be passed through the tube containing the weighing tube and boat.

With the help of this contrivance it was found possible to drive off the ammonic chloride in a current of dry hydrochloric acid, to drive off the excess of acid from the fused magnesic chloride by means of a current of perfectly dry air, and to shut up the pure salt in a weighing bottle without the least possible means of access of a trace of aqueous vapor. The details of the method will be described later; magnesic chloride prepared after this fashion gives a perfectly clear solution in water. Since this problem was solved, attention was now turned to the preparation of materials for the atomic weight determinations.

PREPARATION OF MATERIALS.

The sample of ammonic magnesic chloride which will be hereafter referred to as sample No. 1, was prepared as follows. About five hundred grams of ordinary "C. P." magnesic chloride was saturated with hydrogen sulphide, a small amount of ammonia was added, and the whole was allowed to stand in a warm place for several days. To the supernatant liquid after decantation a small quantity of very pure ammonic oxalate was added. The magnesic chloride thus almost wholly freed from calcium was again decanted; and after more ammonic oxalate had been added, the whole was allowed to stand, and the clear liquid was yet once more decanted. The solution was then evaporated to dryness, and the resulting cake dried in an oven and ignited in a platinum dish. The mixture of magnesic oxide and oxychloride thus formed was washed with the aid of a filter pump for about sixty hours. At the end of this time, although the wash water contained no sodium, the insoluble precipitate was not free from that metal. The precipitate was therefore dissolved in hydrochloric acid, previously distilled in platinum for the purpose, and the solution was filtered. In order to eliminate the sodium, a portion of the magnesium was precipitated by passing into the solution a current of ammonia gas. The precipitate formed by this very wasteful process was washed for several days, at the end of which time it was found to be free from any appreciable traces of sodium and potassium, when tested with the spectroscope.

Ammonic chloride was now prepared by mixing streams of ammonia and hydrochloric acid gas. This gave ammonic chloride mixed probably to a certain extent with various amines, but free from inorganic salts. As the amines must be driven off later, it was not thought worth while to take the trouble of removing them at this stage of the work.

The solution of ammonic chloride thus prepared was added to the solution of magnesic chloride obtained by dissolving the oxychloride in hydrochloric acid in proportions corresponding to formula $Mg_2Cl_2(NH_4)Cl$, and the mixture was carefully evaporated to dryness and gently heated in an oven. It is of course unnecessary to say that all the latter part of this purification was done as far as possible in platinum. The solid cake was powdered in an agate mortar, and placed in a glass stoppered bottle which was kept in a closed jar. The double chloride thus prepared was then tested with the spectroscope, but no impurities could be discovered; and its solution in water was perfectly clear. Tests were made with ammonic oxalate and baric chloride, but in neither case was a precipitate formed on long standing.

The second sample of magnesic chloride was treated in a similar way up to the point where it was necessary to get rid of sodium and potassium. The solution was evaporated to dryness in a platinum dish with the aid of an alcohol lamp, and the resulting cake was gently ignited and then washed for a long time, nothing but platinum being allowed to come in contact with the material from this time forth, and all the heating being done by means of alcohol lamps to avoid the danger of contamination of sulphur from illuminating gas. The oxychloride thus formed was then dissolved in pure hydrochloric acid and filtered. By evaporating down again the magnesium was again rendered insoluble. This process was repeated again and again, until there was no trace of sodium or potassium remaining.

The ammonic chloride necessary for the preparation of the double salt from this second sample of magnesic chloride was prepared by digesting ammonic chloride with nitric acid to destroy the amines.* It was then dried, sublimed several times, recrystallized five or six times from its aqueous solution, and again sublimed in a current of air which had been passed through wash bottles containing respectively a concentrated solution of potash and sulphuric acid. After having been sublimed in this manner about ten or twelve times, it was dissolved in redistilled water and added to the sample of magnesic chloride. The whole was then filtered, evaporated to dryness, partly dehydrated, broken up and placed in a glass stoppered bottle. The usual tests were made as to its purity, but no traces of foreign matter were discovered.

The third sample of magnesic chloride, which was used for the final experiment in the last series, was at first treated in about the same way

* Krüss, Liebig's Annal., CCXXXVIII. 51.

as the others. The precautions taken were somewhat greater, and the fractional precipitation with ammonic oxalate was continued long after the last traces of calcium discoverable by the spectroscope had disappeared from the precipitates of magnesic oxalate. The ammonic magnesic chloride, already very pure, prepared from this sample, was then crystallized eight or ten times, the last six or eight recrystallizations being conducted in platinum. From over a kilogram of magnesic chloride used in the beginning, the portion finally separated out consisted only of a few grams. This sample showed no traces of the sodium line when tested with the spectroscope; indeed, several other samples, obtained from the mother liquors of the purest sample, gave equally satisfactory negative spectroscopic results. Since the magnesic chloride had contained in the first place a very noticeable amount of sodic chloride, the fact of the complete elimination of the impurity seemed a satisfactory indication of the elimination of other foreign materials. The double chloride was dried over an alcohol lamp, and treated in the same manner as the other samples.

PURIFICATION OF SILVER.

No very great labor was expended upon the purification of the first quantity of silver, as the chlorine in magnesic chloride was to be precipitated with an undetermined excess of silver nitrate. Residues were therefore worked up by dissolving silver (obtained by reduction with zinc) in nitric acid, precipitating the metal as chloride, and converting the chloride into metallic silver by means of invert sugar. The reduced silver, after having been fused into buttons, was thoroughly washed and dissolved in nitric acid. The solution of argentic nitrate thus obtained was diluted very much with water, allowed to stand, and filtered just previous to using.

With the second sample, on the other hand, much greater care was taken, as it was designed in this case to ascertain the direct ratio between silver and magnesic chloride. The material came partly from some refined silver, purchased in the market, and partly from some pure silver residues remaining from previous work. The silver was precipitated from a solution of the nitrate with pure hydrochloric acid, and reduced by means of invert sugar and pure sodic hydrate, the sodic hydrate having been previously freed from heavy metals by electrolysis. Both the chloride and reduced silver were very thoroughly washed, the silver was dissolved in pure nitric acid, and the process was repeated. After this cycle of operations had been performed four or five times, the re-

duced silver was fused on a cupel of sugar charcoal before the blowpipe. The resulting button was scrubbed with sand, and made the anode of a weak galvanic circuit in a solution of argentic nitrate prepared from the same silver. The cathode was a piece of pure silver wire, upon which the whole of the silver was deposited in a crystalline mass. The silver crystals were then removed from the solution and fused in a vacuum upon a boat of pure lime,* which was contained in a porcelain tube. Such a boat may be made by lining a porcelain boat with a mixture of three parts of pure lime and one part of pure anhydrous calcic nitrate, and igniting the mixture. The porcelain boat is thus covered with a firm, coherent layer of pure calcic oxide. In order to prevent the possibility of a trace of organic matter distilling off from the rubber stoppers usually used to close such a tube, a set of hollow brass stoppers were made, through which a current of cold water circulated. This latter device is due to a suggestion of Professor Hempel. The construction of this piece of apparatus is evident from the diagram.

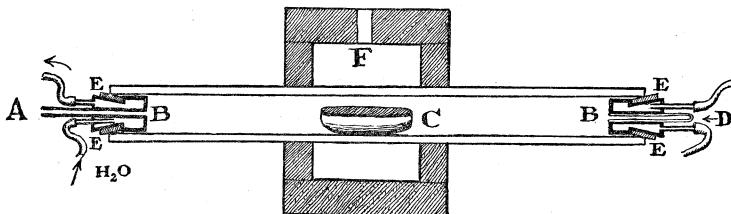


FIG. 2. APPARATUS FOR FUSING SILVER, VERTICAL SECTION.

A is connected with Sprengel pump. **B** = hollow brass stoppers in porcelain tube. **C** = boat of lime containing silver. **D** = "window" for observation. **E E E E** = rubber packing of stopper. **F** = Fletcher furnace.

Of course the button after fusion showed no trace of spitting from contained oxygen. It was scrubbed with distilled water and clean sand, and divided into small pieces by means of a clean steel chisel. The fragments were alternately boiled in strong hydrochloric acid and digested in ammonia water, this process being repeated ten or fifteen times. The silver was finally washed with distilled water and afterwards kept in a desiccator, which was opened only when necessary to weigh out silver for a determination.

A portion of the second sample was treated in the same way, except that in the end it was fused on sugar charcoal before the blowpipe and

* These Proceedings, XXX. 379; XXXI. 173.

cooled in the reducing flame. Particular pains were taken to prevent the absorption of oxygen, and the button did not show the slightest trace of having contained this gas. From this portion wire was prepared of various thicknesses, by means of a draw plate; and the weights of given lengths of these wires were determined, so that small weights could be made with considerable accuracy. Of course the wire was treated in the same fashion as the rest of the silver, in order to remove any iron which might be present on the surface.

The third and fourth samples of silver were prepared in the same manner as the second, the starting point being the pure residues left from the analyses made with previous samples. No qualitative nor quantitative difference could be observed between any of these preparations of silver. Fused upon sugar charcoal, they melted to a clear globule free from any film,—a fact which in itself, according to Stas, is an excellent test of the purity of silver,—and all gave practically the same results in later determinations.

All water used was redistilled with potassic permanganate, some of it being condensed in a platinum condenser and some of it by means of a tube of pure block tin, which was carefully tested in order to prove the absence of an impurity of lead. Considerable quantities upon evaporation in platinum left a scarcely appreciable residue, there being apparently no difference between the water condensed in tin and that in platinum.* The water was prepared as short a time as possible before being used, and was carefully kept in a suitable bottle fitted with a siphon, air being admitted to the bottle through a filter of cotton wool. It was carefully tested for chlorine by means of the nephelometer from time to time.

The sulphuric acid used for the preliminary drying of the gases was the usual "chemically pure" acid of the Laboratory, of a specific gravity of about 1.83. For the final drying this acid was boiled down in platinum.

WEIGHING.

The balance used was a long-armed Becker, sensitive to about one thirtieth of a milligram with the largest load that it was required to carry during the investigation, while the weights were a good set of gold plated ones, which were kept in the balance case under a glass cover. These weights were very carefully compared with one another, and all weighings were, of course, reduced to the vacuum standard. The specific

* See These Proceedings, XXVI. 249; XXX. 380.

gravity of magnesic chloride used for this computation was the value 2.177 determined by Playfair and Joule. Weighing was done by substitution, the object to be weighed being placed on the right-hand pan and balanced by tare weights on the left. In general, the precautions used in the recent work done in this Laboratory upon copper, barium, strontium, and zinc were adhered to with great care.* We are indebted to the Cyrus M. Warren Fund of Harvard University for some of the platinum ware used in the following work.

The atomic weights used in this investigation were as follows:—

| | | | |
|----------|--------|-----------|---------|
| O . . . | 16.000 | Ag. . . . | 107.930 |
| Cl . . . | 35.456 | | |

METHOD OF WORK.

The method of operating may be inferred from the description of the apparatus. The platinum boat, after having been weighed within its weighing bottle, was filled with the double chloride of ammonium and magnesium and placed in position in the ignition tube, resting upon a sort of carriage of platinum foil. The weighing bottle was placed with its stopper in appropriate position in the "bottling tube," as previously described. A current of dry hydrochloric acid gas was then passed through the apparatus and the ignition tube was heated by a suitable arrangement of burners. At first the residual moisture was driven off by the heat and carried away by the stream of gas. When as much water as possible was expelled* in this manner, the heat was slowly increased so that the ammonic chloride commenced to vaporize. It was found that the sublimation commenced before the salt was freed from the last traces of moisture, but an effort was always made, by the very gradual increase of heat, to make this proportion of water as small as possible; and it is probable that the salt was practically anhydrous some time before the last of the ammonic chloride was sublimed. When no further evolution of ammonic chloride could be observed, the heat was increased until the tube and boat were heated to redness, and the magnesic chloride had fused into a clear, colorless limpid liquid. It requires a very excellent piece of combustion tubing to stand the heat necessary to fuse magnesic chloride, and a number of tubes were spoiled during the course of the work. In the first series of determinations the boat was allowed to cool while the current of hydrochloric acid gas was still pass-

* Richards, These Proceedings, XXVI. 240; XXVIII. 1; XXIX. 55; XXX. 369; XXXI. 158.

ing. The tubes containing the boat and weighing bottle were then thoroughly washed out with a current of air dried in an apparatus similar to that used for drying the hydrochloric acid gas, as previously described. After it was certain that all of the acid gas had been displaced, and while the current of air was passing rapidly to prevent any diffusion of moist air back into the apparatus, the bulbs were removed from the farther end of the ignition tube, and the boat was pushed into the bottle in the manner already described. The boat itself remained constant in weight during these operations, showing that the magnesic chloride had not acted upon it.

After weighing, the boat and its contents were placed in a large glass-stoppered Erlenmeyer flask, and the magnesic chloride was dissolved in pure water. The chlorine was precipitated with a dilute solution of argentic nitrate; * and after a thorough shaking the whole was allowed to stand in the dark over night. The argentic chloride was washed by decantation a number of times, with vigorous shaking, and was finally collected upon a Gooch crucible in the usual manner. The precipitate was dried from five to ten hours in an oven, carefully protected from dust and dirt, and weighed. After weighing, the cake of precipitate, together with some adherent asbestos, was removed to a tared porcelain crucible and heated until it began to fuse. The crucible was again weighed, and the loss of weight, if any, noted, and subtracted from the weight of the Gooch crucible and contents. The filtrate, containing a little dissolved argentic chloride, was evaporated down to small bulk and filtered through a very small filter; and the weight of the precipitate was added to the weight of the first portion. In some cases the small amount of argentic chloride present was determined with the nephelometer. †

The wash water from the precipitate collected on the Gooch crucible was also run through a small filter to make sure that no asbestos had been carried away from the crucible in the process of washing; and this correction, when appreciable, was applied in the appropriate place.

The washing and filtration were both performed in dim orange light, which had been suitably tested as to its non-actinic properties. Even after fusing the argentic chloride was almost colorless, showing that only unessential traces had been decomposed by the light.

The result of the first series of five experiments is given below. These

* This solution contained never more than one per cent of silver.

† See These Proceedings, XXX. 385.

determinations were consecutive, except that one determination met with an accident and was not completed.

SERIES I.

| No. of Exp. | Sample of $MgCl_2$ used. | Sample of Ag used. | Weight of $MgCl_2$. | Weight of $AgCl$. | Ratio. $MgCl_2 : 2 AgCl = 100 : n.$ | Atomic Weight of Mg. |
|-------------------|--------------------------|--------------------|----------------------|--------------------|-------------------------------------|----------------------|
| 1 | 1 | 1 | 1.33550 | 4.01952 | 300.975 | 24.368 |
| 2 | 1 | 1 | 1.51601 | 4.56369 | 301.033 | 24.350 |
| 3 | 1 | 1 | 1.32413 | 3.98528 | 300.974 | 24.369 |
| 4 | 1 | 1 | 1.40664 | 4.23297 | 300.928 | 24.384 |
| 5 | 1 | 1 | 1.25487 | 3.77670 | 300.963 | 24.373 |
| Average | | | | | | 24.369 |

A careful consideration of the possible constant errors involved in the foregoing results leads to the belief that the figures found are too high rather than too low, as the presence either of a small amount of water or of oxychloride in the magnesic chloride would tend in this direction.

SECOND SERIES OF DETERMINATIONS.

In order to drive all the subliming ammonic chloride to the farther end of the combustion tube during the ignition, it had been found necessary that the current of gas should be very considerable; and hence it was desirable to construct a piece of apparatus which should deliver the various gases rapidly, but nevertheless as dry as it is possible to obtain them. It was also desirable to work with larger quantities of materials than could be handled in the former apparatus. For these reasons another piece of apparatus was constructed to dry the hydrochloric acid gas; this apparatus contained several flasks of sulphuric acid, three very efficient towers containing the same acid, which was constantly renewed, and a long tube containing resublimed phosphoric pentoxide. One of the towers is shown on the following page. The whole apparatus was fused or ground together, thus wholly avoiding rubber or cork connections.

In the following determinations the boat was allowed to cool in an atmosphere of dry nitrogen, as a further precaution against a possible partial decomposition of the sensitive magnesic chloride. As soon as the

salt had been fused, a current of dry nitrogen was passed into the combustion tube and the hydrochloric acid generator was disconnected. The nitrogen was prepared by passing mixed air and ammonia over rolls of

copper gauze heated to redness, the excess of ammonia being removed by passing the gases through wash bottles containing dilute sulphuric acid; and the nitrogen was dried in a set of towers similar to those used for drying the current of air. When the tube was cool, the current of dry air was turned on, and the tube and its contents washed out as in previous experiments.

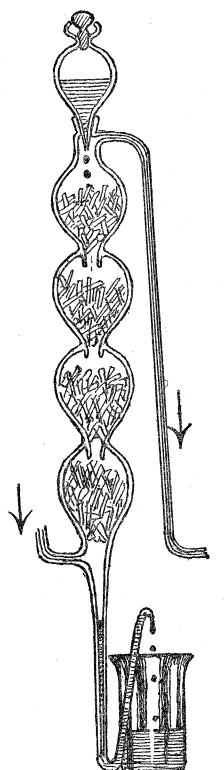
As there were no especial objections against the use of rubber connections and stoppers in the part of the apparatus used for drying the air, several large towers were employed, each filled with crushed pumice stone and saturated with sulphuric acid previous to using. Both air and nitrogen were finally dried by resublimed phosphoric pentoxide. The bottling and combustion tubes were of the same construction as in the former apparatus, except that they were larger.

In the second series, the method of igniting the double salt to obtain the magnesic chloride was the same as in the first; but the method of estimating the amount of chlorine present was different. From the approximate atomic weight of magnesium already found, a calculation was made as to the amount of silver necessary exactly to precipitate the chlorine present in the sample of magnesic chloride taken. This amount

FIG. 3.—ONE OF THE TOWERS
USED FOR DRYING HYDRO-
CHLORIC ACID.

Seventy centimeters high.

of silver was weighed out as nearly as possible, dissolved in nitric acid in an Erlenmeyer flask, provided with a set of bulbs to catch the spray from the evolution of gas, and added to the solution of magnesic chloride contained in a large flask. The flask was thoroughly agitated in the dark, and allowed to stand over night. Fifty cubic centimeters were then withdrawn by means of a pipette, and tested by means of a nephelometer, or apparatus for determining the amount of precipitate from the intensity of the opalescence produced by it. This piece of apparatus was con-



structed for the purpose, and consisted of two rectangular glass cells, with a mirror enclosed in a dark case, so arranged that the column of liquid contained in the lower part of the cells could be viewed horizontally without disturbance from surface reflections. A dark screen was placed at the further end of the cells, and the whole so arranged that light could come to the eye only by reflection from solid particles which might be suspended in the column of liquid inspected. If the liquid was perfectly clear, the field of vision remained black, but an extremely small amount of precipitate produced a very marked change, and the intensity of opalescence was approximately proportional to the amount of precipitate. It was found perfectly easy and certain, by this method, to distinguish the difference between .002 and .003 of a milligram of argentic chloride or between .004 and .005 of a milligram, and larger amounts in proportion. This instrument gave such satisfaction in this research that the method will be worked out for various other reactions, and published later.

The method of using this apparatus was as follows. Twenty-five cubic centimeters of the clear supernatant liquid from the flask containing the well shaken argentic chloride and magnesic nitrate were placed in each cell, five cubic centimeters of a very dilute solution of argentic nitrate being added to one, and five cubic centimeters of a correspondingly dilute solution of ammonic chloride to the other. The silver solution contained one milligram of silver to the cubic centimeter. An unequal depth of cloudiness indicated an excess of either silver or chlorine in the original solution, and accordingly the amount necessary for neutralization was run into the large flask containing precipitate and solution from a burette. The solution was again allowed to stand in the dark with occasional shaking, and after the precipitate had entirely subsided was again tested as before, and this cycle of operations was repeated until the opalescences matched one another.* It will be observed that, if water is added to the cell giving the more dense opalescence until the effect becomes equal on both sides, the amount of dilution will give a means of ascertaining the amount of precipitate in each cell. The appropriate corrections were then applied to the amount of silver taken. Due allowance was made for the slightly diminishing volume of the solution in the flask. The addition of one tenth of a milligram of silver to a litre of solution produced a distinct change in the depth of color observed. After the matching was completed, repeated trials were made with fresh

* For details of this method, see Stas, Mem. Acad. Belg., XLIII. Part II., and Richards, These Proceedings, XXIX. 86; XXX. 385.

portions of the solution to confirm the result ; and as the depth of opalescence as seen in the nephelometer was perfectly flat, without disturbing reflections, the end point could be determined with great precision.

Several results obtained in this manner are given in Series II.

SERIES II.

| No. of Exp. | Sample of $MgVl_2$ used. | Sample of Ag used. | Weight of $Mg Cl_2$. | Weight of Ag. | Ratio. $MgCl_2 : 2 Ag = 100 : n.$ | Atomic Weight of Mg. |
|-------------------|--------------------------|--------------------|-----------------------|---------------|-----------------------------------|----------------------|
| 6 | 1 | 1 | 2.78284 | 6.30284 | 226.490 | 24.395 |
| 7 | 1 | 1 | 2.29360 | 5.19560 | 226.526 | 24.379 |
| 8 | 1 | 2 | 2.36579 | 5.35989 | 226.558 | 24.366 |
| Average | | | | | | 24.380 |

These results, however, do not merit great confidence ; for the apparatus, which had become somewhat complicated, did not work smoothly at first, on account of some minor imperfections which were remedied later. Besides this, careful consideration led to the suspicion that the towers used for drying the air and nitrogen were not efficient enough to remove the last traces of water. Of necessity the towers had to be charged with sulphuric acid an hour or two before their final use, and during that time a large part of the acid drained out of the pumice stone. This surmise was fully confirmed by later experiments ; and since this was the case, the second series must be rejected in the final estimate of the atomic weight.

THIRD SERIES OF DETERMINATIONS.

In order to remedy the most serious defect of the second series, the arrangement for drying the air and nitrogen was much enlarged and improved. By pouring sulphuric acid into the safety funnels at the top of the many towers, from time to time, during the passage of the gas, the glass beads were kept thoroughly saturated during the whole process. The sulphuric acid having reached the bottom of the column drained out of the tubes provided for that purpose into beakers below. It will be seen that by this means the efficiency of the apparatus was far greater than in the previous form. As a test, a very rapid stream of wet air

from a water blast was passed through the apparatus and then through a weighed phosphorus pentoxide bulb for nearly two hours, without the slightest appreciable increase of weight of the pentoxide bulb. The same test was applied to the apparatus for drying the hydrochloric acid gas, with the same result.

With the help of this important addition to the apparatus, another series of determinations was now made. The somewhat lower result of this series is undoubtedly due to the more perfect desiccation of the gases; the agreement of the individual results is still not quite perfect, but the series is undoubtedly far more reliable than the second.

SERIES III.

| No. of Exp. | Sample of $MgCl_2$ used. | Sample of Ag used. | Weight of $MgCl_2$. | Weight of Ag. | Ratio, $MgCl_2 : 2Ag = 100 : n$ | Atomic Weight of Mg. |
|-------------------|--------------------------|--------------------|----------------------|---------------|---------------------------------|----------------------|
| 9 | 1 | 2 | 1.99276 | 4.51554 | 226.597 | 24.349 |
| 10 | 1 | 2 | 1.78870 | 4.05256 | 226.565 | 24.363 |
| 11 | 1 | 2 | 2.12832 | 4.82174 | 226.551 | 24.369 |
| 12 | 2 | 2 | 2.51483 | 5.69714 | 226.542 | 24.373 |
| 13 | 2 | 3 | 2.40672 | 5.45294 | 226.571 | 24.360 |
| 14 | 2 | 3 | 1.95005 | 4.41747 | 226.531 | 24.377 |
| Average | | | | | | 24.365 |

FOURTH AND FINAL SERIES OF DETERMINATIONS.

The apparatus was now put in the best possible order, and the phosphorous pentoxide tubes were recharged, in order to make ready for a series of determinations in which the very highest exactness was to be aimed at. The purest samples of material were used, and all other precautions, learned from previous work, were taken to insure accuracy. The following determinations were consecutive, with the exception of one between Nos. 15 and 16, which was spoiled by a slight accident.

These results agree with one another as well as could possibly be expected, for the difference between the extremes in the last series corresponds to a difference of only one tenth of a milligram in the weight of the magnesic chloride. Since two wholly distinct samples of this salt

SERIES IV.

| No. of Exp. | Sample of $MgCl_2$ used. | Sample of Ag used. | Weight of $MgCl_2$. | Weight of Ag. | Ratio. $MgCl_2 : 2 Ag = 100 : n.$ | Atomic Weight of Mg. |
|------------------------|--------------------------|--------------------|----------------------|---------------|-----------------------------------|----------------------|
| 15 | 2 | 3 | 2.03402 | 4.60855 | 226.578 | 24.360 |
| 16 | 2 | 3 | 1.91048 | 4.32841 | 226.562 | 24.364 |
| 17 | 2 | 3 | 2.09932 | 4.75635 | 226.566 | 24.362 |
| 18 | 2 | 2 | 1.82041 | 4.12447 | 226.568 | 24.362 |
| 19 | 2 | 2 | 1.92065 | 4.35151 | 226.565 | 24.363 |
| 20 | 3 | 4 | 1.11172 | 2.51876 | 226.564 | 24.363 |
| Average | | | | | | 24.362 |
| Extreme difference . . | | | | | | 0 004 |

and three wholly distinct samples of silver were used in this series, we may conclude that all ordinary accidental errors had been eliminated; and in a critical discussion of the result we may limit ourselves to the consideration of the possible constant errors of the process.

The most serious objection to the method is, of course, the possible retention of water, of magnesic oxychloride, or of ammonic chloride by the magnesic salt.

With regard to the first two difficulties, it need only be said that the gases used for drying the magnesic chloride were as dry as present possibilities permit them to be made. The phosphorus pentoxide in the last drying tube showed no trace of liquefaction at the close of the research, but seemed to be as light and powdery as at first, in spite of the fact that several hundred litres of gas had been passed over it. Any trace of oxygen, as well as of aqueous vapor, was excluded from the hot salt; for the hydrochloric acid gas was replaced by nitrogen, and this was driven out in its turn by dry air only after the tube had cooled. A means of proving absolutely that no water remained does not exist; but it is extremely hard to see how water could have gained access to the carefully guarded magnesic chloride.

The fact that every sample of magnesic chloride used in the last series gave an absolutely clear and transparent solution in water is additional evidence of much weight; for a very small trace of oxychloride would

have shown itself in opalescence. As a proof of this it may be stated that in experiment No. 12 of Series III. there was a perceptible cloudiness upon the solution of the magnesic chloride in water, owing to a known access of a trace of aqueous vapor, caused by a momentary stoppage of the current of nitrogen. This result is, however, scarcely at all different from the others.

With regard to the possible retention of ammonic chloride by the magnesium salt, it may be said: first, that none could be detected by means of a Nessler solution; and, secondly, that even if a small amount had been retained, it would have made but a very slight difference in the final result.

Our result is essentially the same, no matter whether the chlorine is weighed as argentic chloride (Series I.), or the amount of silver necessary to precipitate it is found (Series III. and IV.). This fact is satisfactory evidence that that silver and chlorine were both pure, as well as that no magnesic chloride was occluded by the argentic chloride. Thus: —

From the ratio $2 \text{AgCl} : \text{MgCl}_2$ (Series I.), $\text{Mg} = 24.369$.

“ “ $2 \text{Ag} : \text{MgCl}_2$ (Series III.), $\text{Mg} = 24.365$.

“ “ $2 \text{Ag} : \text{MgCl}_2$ (Series IV.), $\text{Mg} = 24.362$.

Upon comparing these figures with the older ones, they are seen to agree surprisingly with Marignac's value obtained from work upon magnesic oxide and sulphate ($\text{Mg} = 24.37$). Burton and Vorce's syntheses of magnesic oxide gave a lower value for magnesium (24.28); but if these were corrected for a probable amount of gases in the magnesic oxide, the result would probably be close to the present one. The analytical chemist should not forget that the value 24.36 is one and a half per cent higher than the round number 24, which has been so commonly accepted.

For reasons which must be manifest to any careful reader of the foregoing paper, we accept the value given by the fourth and last of our series as representing the most probable atomic weight of magnesium. It remains only to state this result in terms of the usual unfortunately varying standards of reference used by the scientific world.

If $O = 16.000$, $\text{Mg} = 24.362$.

If $O = 15.96$, $\text{Mg} = 24.301$.

If $O = 15.88$, $\text{Mg} = 24.179$.